Synthesis and Structural Characterization of Monomeric Selenolato Complexes of Zinc, Cadmium, and Mercury

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The synthesis and characterization of homoleptic zinc(II), cadmium(II), and mercury(II) selenolates incorporating the intramolecularly chelating oxazoline ligand are described. The derivatives, M[Se(Ox)]$_2$ [M = Zn (**1**), Cd (**2**), Hg (**3**); Ox = 2-(4,4-dimethyl-2-oxazolinyl)benzene], were prepared in good yield via the metathesis reactions of MCl$_2$ with a lithium areneselenolate, OxSe$^-$Li$^+$. The mercury complex **3** was also synthesized by treating the corresponding diselenide with elemental mercury. The complexes are quite stable and highly soluble in common nonpolar organic solvents. X-ray diffraction results show that the complexes are monomeric in the solid state. The geometry around the metal ion in all complexes is found to be distorted tetrahedral. The crystal structure of Zn[Se(Ox)]$_2$ (**1**) shows that the complex is "helically" chiral and enantiomerically pure. The spontaneous splitting of the racemates indicates the solubility differences between the racemates and pure enantiomers. ^{1}H, ^{13}C, and ^{77}Se NMR measurements indicate that complex **1** retains its "helical" structure in solution. Crystal data (Mo Kα; 293(2) K) are as follows: **1**, monoclinic space group $P2_1$, $a = 9.3900(12)$ Å, $b = 11.618(2)$ Å, $c = 10.8822(14)$ Å, $\beta = 98.245(8)°$, $Z = 2$; **2**, orthorhombic space group $Pbca$, $a = 12.777(6)$ Å, $b = 17.841(10)$ Å, $c = 21.010(8)$ Å, $Z = 8$; **3**, monoclinic space group $P2_1/c$, $a = 9.087(2)$ Å, $b = 11.889(2)$ Å, $c = 22.456(4)$ Å, $\beta = 98.780(13)°$, $Z = 4$.

Introduction

Intramolecular coordination in organoselenium chemistry has attracted considerable current attention.[1] Recent studies on intramolecularly stabilized organoselenium compounds show that the Se···N intramolecular interactions play an important role not only in the catalytic antioxidant activity of these compounds[2] but also in their application as reagents in synthetic organic chemistry.[3] The application of intramolecular coordination has been extended to the synthesis of novel organoselenium ligands.[4] More recently, the intramolecular coordination has been used for the isolation of monomeric metal selenolates,[4a,5] in particular, the isolation of group 12 metal (Zn, Cd, Hg) selenolates which are generally polymeric through bridging by the chalcogenolate ligands. Brennan and co-workers have isolated a range of metal selenolates using the pyridineselenolate ligand where the two heteroatom donors create a variety of potential bonding modes.[6] Although the Cd and Hg selenolates were polymeric, the compounds were volatile and sublimed

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without decomposition at relatively low temperatures and decomposed at higher temperature to give the desired MSe.[6a]

In continuation of our work on intramolecularly coordinated organochalcogens, [1h, 7] we recently isolated and structurally characterized several stable chiral and achiral organoselenenyl halides, RSeX (X = Cl, Br, I), using 4,4-dimethyl-2-phenyloxazoline and 4-ethyl-2-phenyloxazoline in which the Se⋯N intramolecular interactions are very strong.[8] Recently, we reported the preparation of some stable monomeric mercury selenolates using ortho-chelating *N*, *N*-dimethylaminoaryl ligands.[9] However, the monomeric zinc and cadmium selenolates could not be isolated. We have now succeeded in preparing the isolable, well-characterized examples of zinc, cadmium, and mercury selenolato complexes by using a more rigid 4,4-dimethyl-2-phenyloxazoline substrate. Our interest in selenium derivatives of phenyloxazoline stems from the following major attractive characteristics of the oxazoline skeleton. They can effect efficient chirality transfer from the heterocycle to newly formed bonds, thereby generating new chiral centers with high asymmetric induction.[10] Oxazolines have also been found in many naturally occurring siderophore chelating agents, like mycobactine, parabactine, and vibriobactine.[11] In these cases, they show extremely strong coordination to the metal centers, illustrating the high chelating ability of this moiety.[12]

In this paper, we also describe the use of the phenyloxazoline ligand to prepare a novel "helically" chiral zinc selenolate (**1**) and its spontaneous resolution. Although many double- and triple-helical metal complexes have been reported, [13] the simpler "monohelical" metal complexes have received much less attention. The structurally characterized "monohelical" complexes include, those of ten-coordinate europium(III), [14] seven-coordinate cobalt(II), [15] and five-coordinate silver(I).[16] Structurally characterized "monohelical" complexes of zinc are very rare,[17] and this is the first example, to the best of our knowledge, where the "helical" chirality is observed in a four-coordinate zinc selenolate complex. The room-temperature NMR (^{1}H, ^{13}C, ^{77}Se) spectra of the Cd (II) and Hg(II) analogues of **1** are not indicative of "helicity", but the Cd(II) complex shows chirality at low temperatures.

Experimental Section

General Procedures. All reactions were carried out under nitrogen or argon using standard vacuum-line techniques. Solvents were purified by standard procedures[18] and were freshly distilled prior to use. Mercury and $ZnCl_2$ were purified prior to use.[18] Commercially available $CdCl_2$ and $HgCl_2$ were used as received. Melting points were recorded in capillary tubes and are uncorrected. ^{1}H, ^{13}C, and ^{77}Se NMR spectra were obtained at 300, 75.42, and 57.22 MHz, respectively, in $CDCl_3$ on a Varian VXR 300S spectrometer. Chemical shifts are cited with respect to $SiMe_4$ as internal (^{1}H and ^{13}C) and Me_2Se (^{77}Se) as external standard. Elemental analyses were performed on a Carlo-Erba model 1106 elemental analyzer. Fast atom bombardment (FAB) mass spectra were recorded at room temperature on a JEOL SX 102 DA-6000 mass spectrometer/data system using xenon (6 kV, 10 mV) as the bombarding gas. The acceleration voltage was 10 kV, and *m*-nitrobenzyl alcohol was used as the matrix with positive-ion detection. In case of isotopic patterns, the value given is for the most intense peak.

Synthesis of Zn[Se(Ox)]$_2$ (1). To a solution of 4,4-dimethyl-2-phenyloxazoline (1.75 mL, 1.79 g, 10 mmol) in dry hexane (50 mL) was added a 1.6 M solution of *n*-BuLi in hexane (6.8 mL, 11 mmol). After 1 h of stirring at room temperature, a white precipitate of the lithiated compound (OxLi) was obtained. The supernatant solvent was removed with a syringe. The white precipitate was dissolved in dry ether, the solution was cooled to 0 °C, and selenium powder (0.8 g, 10 mmol) was added. After 2 h of stirring at this temperature, anhydrous $ZnCl_2$ (0.68 g, 5 mmol) was added, and stirring was continued for an additional 1 h at 0 °C and 18 h at room temperature. The resulting solution was filtered through Celite, and the solvent was evaporated to give a yellow compound. The compound was recrystallized from a chloroform−hexane (1:1) mixture to give **1**. The spontaneous resolution of the racemate was observed during the crystallization process. The crude yellow compound (1.43 g) was dissolved in chloroform (20 mL), and hexane (20 mL) was added. Slow evaporation of the solvent at room temperature afforded the crystals of the two enantiomorphs. Yield: 1.29 g (45%). Mp: 221−223 °C. Anal. Calcd for $C_{22}H_{24}N_2O_2Se_2Zn$: C, 46.16; H, 4.23; N, 4.90. Found: C, 46.85; H, 4.88; N, 4.88. ^{1}H NMR (300 MHz, $CDCl_3$; δ, ppm): 1.10 (s, 6H, $-CH_3$), 1.58 (s, 6H, $-CH_3$), 4.00−4.20 (dd, 4H, $-CH_2-$), 7.05−7.14 (m, 4H, Ar H), 7.67−7.70 (m, 2H, Ar H) 7.99−8.02 (m, 2H, Ar H). ^{77}Se NMR ($CDCl_3$; δ, ppm): 14.65 (s), 31.19 (s). ^{13}C NMR ($CDCl_3$; δ, ppm): 26.93, 28.66, 66.98, 69.04, 77.52, 78.68, 113.86, 123.60, 125.99, 130.60, 131.27, 132.18, 133.05, 139.07, 141.33, 168.08, 168.57. MS: *m*/*z* 890 ($C_{33}H_{36}N_3O_3Se_3Zn_2$), 826 ($C_{33}H_{36}N_3O_3Se_3Zn$), 572 ($M^+$, $C_{22}H_{24}N_2O_2Se_2Zn$), 509 ($C_{22}H_{24}N_2O_2Se_2$), 429 ($C_{22}H_{24}N_2O_2Se$), 318 ($C_{11}H_{12}NOSeZn$), 254 (100%, $C_{11}H_{12}NOSe$). $[\alpha]^{25}_{D} = -4.079$ (*c* 0.95, $CHCl_3$).

Synthesis of Cd[Se(Ox)]$_2$ (2). Compound **2** was prepared by following the method described for **1** using 1.79 g (1.75 mL, 10 mmol) of 4,4-dimethyl-2-phenyloxazoline, 6.8 mL (11 mmol) of 1.6 M solution of *n*-BuLi, and 0.917 g (5 mmol) of anhydrous $CdCl_2$. The crude product was recrystallized from a chloroform−hexane (1:1) mixture. Yield: 1.60 g (52%). Mp: 198−200 °C. Anal. Calcd for $C_{22}H_{24}N_2O_2Se_2Cd$: C, 42.70; H, 3.88; N, 4.52. Found: C, 42.39; H, 4.21; N, 4.46. ^{1}H NMR (300 MHz, $CDCl_3$; δ, ppm): 1.21 (s, br, 12H, $-CH_3$), 4.08 (s, 4H, $-CH_2-$), 7.05−7.15 (m, 4H, Ar H), 7.67−7.71 (m, 2H, Ar H), 7.99−8.03 (m, 2H, Ar H). ^{77}Se NMR ($CDCl_3$; δ, ppm):

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Table 1. Crystal Data and Structure Refinement Details for **1**−**3**

	1	**2**	**3**
empirical formula	$C_{22}H_{24}N_2O_2Se_2Zn$	$C_{22}H_{24}N_2O_2Se_2Cd$	$C_{22}H_{24}N_2O_2Se_2Hg$
fw	571.72	618.75	706.94
crystal system	monoclinic	orthorhombic	monoclinic
space group	$P2_1$	Pbca	$P2_1/c$
a (Å)	9.3900(12)	12.777(6)	9.087(2)
b (Å)	11.618(2)	17.841(10)	11.889(2)
c (Å)	10.8822(14)	21.010(8)	22.456(4)
α (deg)	90	90	90
β (deg)	98.245(8)	90	98.780(13)
γ (deg)	90	90	90
V (Å^3)	1174.9(3)	4789(4)	2397.4(7)
Z	2	8	4
D_{calcd} (Mg/m^3)	1.616	1.716	1.959
temp (K)	293(2)	293(2)	293(2)
λ (Å)	0.710 73	0.710 69	0.710 73
abs coeff (mm^{-1})	4.162	3.971	9.475
no. of obsd reflns [$I > 2\sigma(I)$]	3055	4185	5265
final $R(F)$ [$I > 2\sigma(I)$][b]	0.0444,	0.0682	0.0573
$R_w(F^2)$ indices [$I > 2\sigma(I)$][b]	0.0839	0.1439	0.1321
absolute structure param[29]	−0.01(2)		
data/restraints/params	3047/1/291	4185/−/266	5265/−/291
goodness of fit on F^2	1.01	1.11	1.02

[a] Additional crystallographic details are given in the Supporting Information. [b] Definitions: $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w(F^2) = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_c^2)^2]\}^{1/2}$.

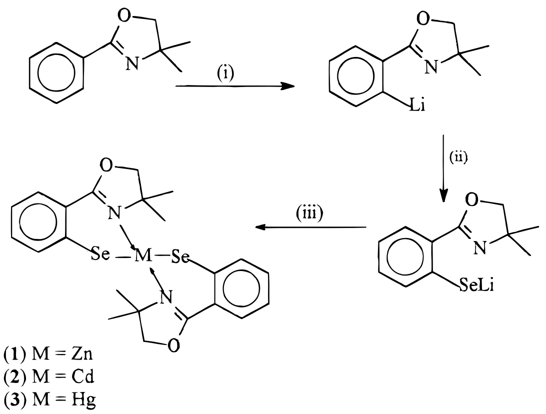
−7.56 (s). ^{13}C NMR (CDCl$_3$; δ, ppm): 28.07, 68.59, 78.53, 124.27, 128.08, 130.85, 131.52, 137.18, 139.48, 167.53. MS: m/z 985 ($C_{33}H_{36}N_3O_3Se_3Cd_2$), 619 (M$^+$, $C_{22}H_{24}N_2O_2Se_2Cd$), 429 ($C_{22}H_{24}N_2O_2Se$), 366 ($C_{11}H_{12}NOSeCd$), 254 (100%, $C_{11}H_{12}NOSe$).

Synthesis of Hg[Se(Ox)]$_2$ (3). Method A. Compound **3** was prepared by following the method described for **1** using 1.79 g (1.75 mL, 10 mmol) of 4,4-dimethyl-2-phenyloxazoline, 6.8 mL (11 mmol) of 1.6 M solution of n-BuLi, and 1.358 g (5 mmol) of anhydrous HgCl$_2$. The crude product was recrystallized from a chloroform−hexane (1:1) mixture. Yield: 2.12 g (60%). Mp: 140−142 °C. Anal. Calcd for $C_{22}H_{24}N_2O_2Se_2Hg$: C, 37.37; H, 3.39; N, 3.96. Found: C, 37.43; H, 3.75; N, 3.96. ^{1}H NMR(300 MHz, CDCl$_3$; δ, ppm): 1.17 (s, 12H, −CH$_3$), 3.99 (s, 4H, −CH$_2$−), 7.13−7.26 (m, 4H, Ar H), 7.63−7.67 (m, 2H, Ar H), 7.91−7.94 (m, 2H, Ar H). ^{77}Se NMR (CDCl$_3$; δ, ppm): 115.6 (s). ^{13}C NMR (CDCl$_3$; δ, ppm): 28.21, 68.91, 78.80, 125.78, 130.28, 130.54, 130.71, 132.68, 138.24, 164.08. MS: m/z 709 (M$^+$, $C_{22}H_{24}N_2O_2Se_2Hg$), 507 ($C_{22}H_{24}N_2O_2Se_2$), 429 ($C_{22}H_{24}N_2O_2Se$), 254 (100%, $C_{11}H_{12}NOSe$).

Method B. To a stirred solution of 4,4-dimethyl-2-oxazolinylphenyl diselenide[8] (0.506 g, 1 mmol) in methanol (50 mL) was added an excess of mercury (1 g, 5 mmol) at room temperature. The reaction mixture was stirred for 2 days to give an almost colorless solution. This was filtered through a Celite-padded filter frit to remove the unreacted mercury. The filtrate was concentrated to give a colorless crystalline product (0.64 g). This was recrystallized from a chloroform−methanol mixture to give colorless crystals of **3** (0.60 g, 85%).

X-ray Crystallographic Studies. The diffraction measurements for complexes **1** and **3** were performed at room temperature (295 K) on a Siemens R3m/V diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.7170$ Å). An Enraf-Nonius CAD4 diffractometer was used for complex **2**. The unit cell was determined from 25 randomly selected reflections using the automatic search index and least-squares routine. For **1**, the θ range for data collection was from 2.19 to 30.00° whereas for **2** and **3** it ranged between 2.19 and 24.96° and between 2.27 and 27.50°, respectively. The index ranges for **1** were $-13 \le h \le 0$, $-16 \le k \le 0$, $-15 \le l \le 15$ while for **2** and **3** they were $0 \le h \le 15$, $0 \le k \le 21$, $0 \le l \le 24$ and $-11 \le h \le 0$, $-15 \le k \le 0$, $-28 \le l \le 29$, respectively. The data were corrected for Lorentz, polarization, and absorption effects. The maximum and minimum transmission values of the correction factors for compound **1** (dimensions 0.22 × 0.68 × 0.58 mm) were 0.732 87 and 0.272 74 and for **3** (0.35 × 0.6 × 0.5 mm) were 0.3460 and 0.0678, respectively. The data were monitored by measuring two standard reflections every 60 min of X-ray exposure time. The structure for **2** was solved by routine heavy-atom (using SHELXS 86[19]) and Fourier methods and refined by full-matrix least squares with the non-hydrogen atoms anisotropic and hydrogens having fixed isotropic thermal parameters of 0.07 Å^2 using the SHELXL 93 program.[20] The structures **1** and **3** were solved and refined using the SHELXTL program.[21] The hydrogens were partially located from difference electron-density maps and the rest were fixed at calculated positions. Scattering factors were from common sources.[22] Some details of the data collection and refinement are given in Table 1.

Scheme 1. Synthesis of M(II) Complexes[a]



[a] Reagents and conditions: (i) n-BuLi, hexane, rt, 1 h; (ii) Se powder, ether, 0 °C, 2 h; (iii) anhydrous, MCl$_2$, 0 °C, 1 h, and rt, 18 h.

Results and Discussion

Monomeric selenolates. Synthesis of the selenolate complexes was approached by the metathesis reaction of the lithium areneselenolate with the corresponding MCl$_2$ in ether (Scheme 1). The lithium areneselenolate, OxSe$^-$Li$^+$, was easily prepared

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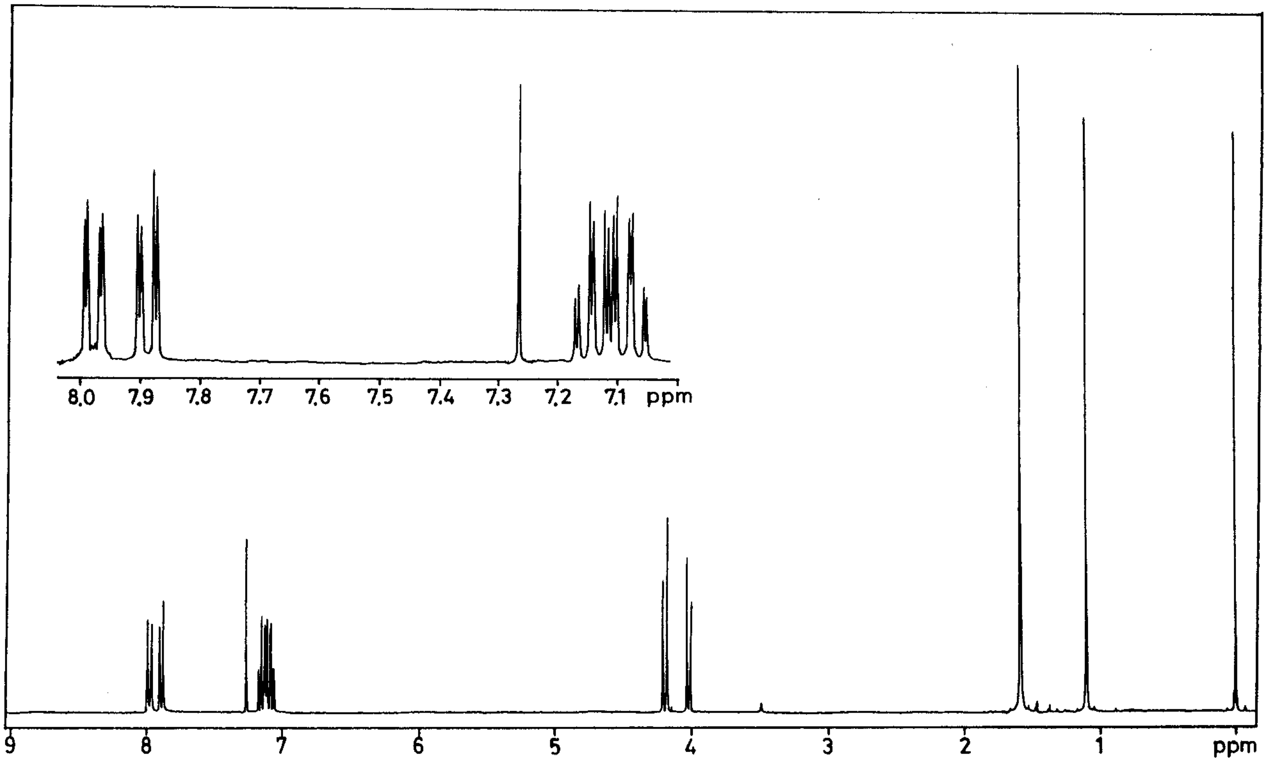

Figure 1. Room-temperature ^{1}H NMR spectrum of **1** ($CDCl_3$, 300 MHz).

by the direct low-temperature metalation of 4,4-dimethyl-2-phenyloxazoline with *n*-BuLi in *ether* followed by the addition of selenium powder.[23] However, the reaction of the lithium areneselenolate thus obtained with MCl_2 failed to give the desired complexes in pure form. Alternatively, the pure lithiated compound, OxLi, was prepared by the direct metalation of the oxazoline with *n*-BuLi in *hexane* at room temperature. This reaction afforded a white precipitate of the lithiated compound whereas the side products remained in solution. The supernatant solvent was removed with a syringe and fresh *ether* added. The lithium selenolate was then obtained by the reaction of OxLi with elemental selenium in *ether* at 0 °C.

The 2:1 molar reaction of $OxSe^-Li^+$ and MCl_2 in diethyl ether afforded the desired products in excellent yields. The mercury complex (**3**) was also prepared by the reaction of the diselenide (Ox_2Se_2) with elemental mercury. Yields of the three compounds generally range from 45% to 85% after crystallization from a chloroform−hexane mixture. The yield of complex **3** was much better when the diselenide was used as the starting material.

Complex **1**, obtained as a yellow solid, shows some interesting features. The complex affords two types of crystals: plates and needle-shaped crystals due to spontaneous crystallization of the enantiomers (vide infra). The racemate of complex **1** shows very good solubility in diethyl ether, but the solubility is reduced for the enantiomers in the same solvent. The complexes have excellent solubility in both nonpolar and slightly polar solvents. They are, however, almost insoluble in highly polar solvents such as DMSO and methanol.

NMR Spectroscopic Studies. The X-ray crystal structures show unambiguously the formation of the monomeric selenolates in the solid state, but, if the complexes are to be considered as true examples of monomers, it remains essential to show that they are stable in solution and are not involved in any association process which leads to dimeric, trimeric, or polymeric products. To this end, we have studied in detail the ^{1}H, ^{13}C, and ^{77}Se NMR spectra in $CDCl_3$ to investigate the solution behavior of the complexes. The room-temperature ^{1}H NMR spectrum of complex **1** contains a well-resolved AB doublet-of-doublets for the methylene protons, indicative of an inequivalence of the geminal protons in the molecule (Figure 1). The AB pattern implies that the strong coordination of the imine “hard” nitrogen with “hard” zinc(II) removes the erstwhile enantiotopic nature of the methylene protons. The protons become diastereotopic, resulting in chirality of the complex.[17b] The inequivalence of the methylene group protons and two methyl group protons even at 55 °C indicates a strong coordination of the nitrogen to the metal center and retention of the “helicity” even at higher temperatures.

The room-temperature ^{1}H NMR spectrum of **2** consists of a singlet for the methylene protons and another singlet for the methyl protons. However, the signal for the methyl protons is broad, and this shows that the complex is probably not rigid at room temperature. At −60 °C, the methyl protons give rise to two singlets and the methylene protons give an AB quartet (Figure 2.). This clearly indicates the existence of a helical arrangement of atoms around the metal center due to the stereorigidity of the ligands at low temperature. When the solution is heated to 55 °C, the broad signal observed for the methyl protons at room temperature becomes a sharp singlet, thus indicating an exchange between the helical and nonhelical arrangements. The mercury selenolate (**3**) displayed a straightforward, unremarkable ^{1}H NMR spectrum. The signals for the methylene and methyl protons are sharp singlets. Since the exchange between helical and nonhelical arrangements is very fast, the splitting of the signals due to chirality could not be detected even at −60 °C. At this temperature, only slight broadening of the signals was observed. The same behavior is also reflected in the ^{13}C NMR spectra.

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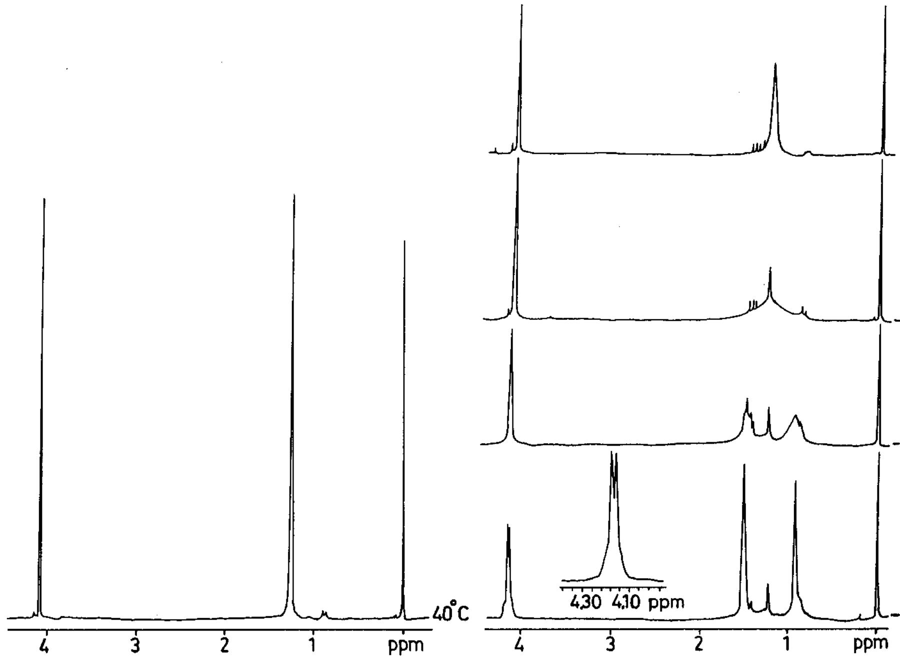

Figure 2. Variable-temperature ^{1}H NMR ($CDCl_3$, 300 MHz) spectra (in part only) of **2**. At −60 °C, the signals due to the $-CH_2-$ and $-CH_3$ protons split into an AB quartet and two singlets, respectively.

To confirm the monomeric structure in solution, we have recorded ^{77}Se NMR spectra for all the complexes as ^{77}Se is a very sensitive NMR nucleus and it is easily influenced by its chemical environment. The ^{77}Se chemical shifts for the complexes are in the range δ −7.56 to 115.6 ppm. The chemical shifts for all the complexes are shifted upfield compared with that of the diselenide (454.79 ppm). The significant upfield shift of the ^{77}Se resonances of complexes **1**−**3** is due to filled d orbitals (d^{10}) which cannot accept electron density from the $OxSe^-$ ligand.[24, 25] Interestingly, the ^{77}Se resonance of the Cd(II) complex (−7.56 ppm) is shifted upfield more than its first- or third-row metal counterparts (31.19 and 14.65 ppm for Zn(II) and 115.6 ppm for Hg(II) complex). This is due to a better overlap of the orbitals of Se (where 5s and 4d are unoccupied orbitals) and cadmium (where 5s and 4d orbitals are being filled).[25] For complex **1**, two signals appear at 31.19 and 14.65 ppm relative to Me_2Se and indicate nonequivalence of the two selenium atoms present in the complex. The difference in the selenium nuclei is mainly due to the spatial arrangement of the two selenium atoms[26] around the metal ion. For the Cd and Hg complexes, the signals which appear at −7.56 and 115.6 ppm, respectively, are indicative of the equivalence of the selenium nuclei and hence nonhelical environment.

From the above observations it is clear that all the complexes are monomeric in solution, which is consistent with the solid state structures. There is no indication of the ligand association which is generally observed for the metal selenolates in solution.[27]

Mass Spectroscopic Studies. Surprisingly the mass spectra of compounds **1** and **2** are indicative of the presence of both monomeric and dimeric species in the gas phase.**1**: $Zn(SeOx)_2^+$, *m/z* 572; $Zn_2(SeOx)_3^+$, *m/z* 890. **2**: $Cd(SeOx)_2^+$, *m/z* 619; $Cd_2(SeOx)_3^+$, *m/z* 985. The mass spectrum of compound **3** shows no peak higher than the expected molecular mass, which is in agreement with the crystal structure. The primary organic product Ox−Se−Ox was observed in all the complexes and indicates the formation of MSe under mass spectroscopic conditions. The molecular ion peaks and the peaks due to other fragments containing Se and M exhibit the expected isotope patterns.

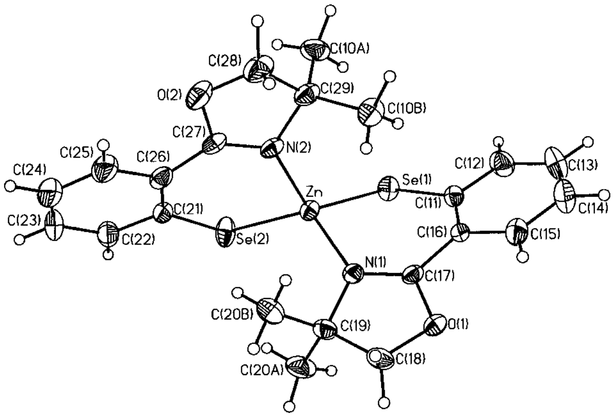

Figure 3. Crystal structure of the monomeric Zn(II) complex (**1**).

Molecular Structure of Compound 1. Complex **1** crystallizes in a chiral space group $P2_1$. Crystals of compound **1** belong to the monoclinic system. Figure 3 depicts an ORTEP[28] view of the molecule. Although tetrahedral complexes with AB type chelate ligands are expected to be chiral, to our knowledge, no optically pure chiral tetrahedral zinc complexes have been reported so far (generally they crystallize as racemates). It is worth noting that helically chiral zinc complexes with multidentate ligands have been the center of attention in the recent past, [17] and complex **1** is the first example of a helically chiral zinc complex derived from a bidentate selenolate ligand. Refinement of the Flack enantiopole parameter[29] led

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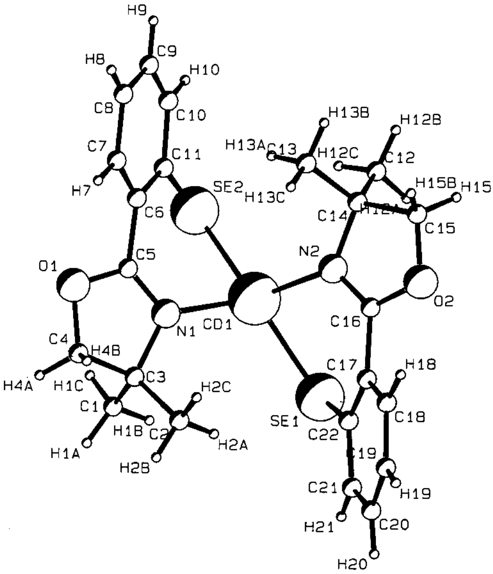

Figure 4. Crystal structure of the monomeric Cd(II) complex (**2**).

Table 2. Significant Bond Lengths (Å) and Angles (deg) for **1**

Zn−N(2)	2.046(7)	Zn−N(1)	2.051(5)
Zn−Se(2)	2.3749(12)	Zn−Se(1)	2.3823(13)
Se(1)−C(11)	1.905(7)	Se(2)−C(21)	1.875(9)
O(1)−C(17)	1.362(8)	O(1)−C(18)	1.420(10)
O(2)−C(27)	1.354(10)	O(2)−C(28)	1.425(13)
N(1)−C(17)	1.302(9)	N(1)−C(19)	1.472(10)
N(2)−C(27)	1.290(11)	N(2)−C(29)	1.481(12)
N(2)−Zn−N(1)	106.6(2)	N(2)−Zn−Se(2)	97.3(2)
N(1)−Zn−Se(2)	122.1(2)	N(2)−Zn−Se(1)	122.4(2)
N(1)−Zn−Se(1)	96.7(2)	Se(2)−Zn−Se(1)	113.49(5)
C(11)−Se(1)−Zn	100.1(2)	C(21)−Se(2)−Zn	102.6(3)
C(17)−O(1)−C(18)	106.2(6)	C(27)−O(2)−C(28)	107.2(7)
C(17)−N(1)−C(19)	109.0(6)	C(17)−N(1)−Zn	124.6(5)
C(19)−N(1)−Zn	126.3(5)	C(27)−N(2)−C(29)	109.4(7)
C(27)−N(2)−Zn	127.0(6)	C(29)−N(2)−Zn	123.5(6)

to a value of ∼0, thus confirming the enantiomeric purity of the crystal.

The complex is monomeric with the zinc atom coordinated to two nitrogen and to two selenium atoms, forming a distorted tetrahedron. Significant bond lengths and angles are given in Table 2. The average Zn−Se bond distance 2.378(1) Å is comparable to those reported for $[\mathrm{Zn(SeC_6H_2Bu^t_3\text{-}2,4,6)_2(OSC_4H_8)}]$[30] [2.313(3) Å] and $[\mathrm{Zn(SeC_6H_2Bu^t_3\text{-}2,4,6)_2(CNBu^t)_2}]$[31] [2.380(3) Å]. The average Zn−N bond distance 2.048(6) Å is comparable to that observed for $[\mathrm{Zn\{Bu^t_2P(Se)NPr^i\}_2}]$ [1.981(3) Å][32] and also those reported for zinc and typical N-donor ligands which normally range from 2.04 to 2.14 Å. The average Se−Zn−N chelate bite angle is 97.0(2)° and this is considerably larger than that reported for $[\mathrm{Zn\{Bu^t_2P(Se)NPr^i\}_2}]$ [81.37(9)°].[32] The larger bite angle leads to relatively smaller Se−Zn−Se and N−Zn−N angles of 113.49(5) and 106.6(2)°, respectively. The corresponding values for $[\mathrm{Zn\{Bu^t_2P(Se)NPr^i\}_2}]$ are 120.00(3) and 136.16(3)°, respectively. The interplanar angle between Se−Zn−Se and N−Zn−N is 72.1(3)°.

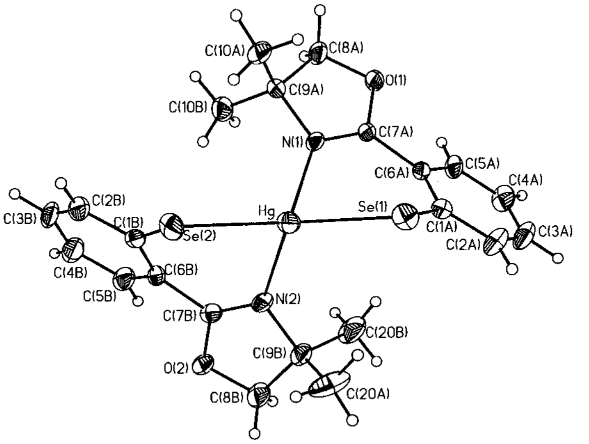

Figure 5. Crystal structure of the monomeric Hg(II) complex (**3**).

Table 3. Significant Bond Lengths (Å) and Angles (deg) for **2**

Cd(1)−N(1)	2.276(9)	Cd(1)−N(2)	2.278(9)
Cd(1)−Se(1)	2.549(2)	Cd(1)−Se(2)	2.552(2)
Se(2)−C(11)	1.945(11)	Se(1)−C(22)	1.935(12)
O(1)−C(5)	1.358(13)	O(1)−C(4)	1.447(14)
O(2)−C(16)	1.361(14)	O(2)−C(15)	1.427(14)
N(1)−C(5)	1.270(14)	N(1)−C(3)	1.507(14)
N(2)−C(16)	1.268(14)	N(2)−C(14)	1.500(13)
N(1)−Cd(1)−N(2)	105.0(3)	N(2)−Cd(1)−Se(2)	118.0(2)
N(1)−Cd(1)−Se(1)	117.8(2)	N(2)−Cd(1)−Se(1)	89.8(2)
N(1)−Cd(1)−Se(2)	89.1(2)	Se(1)−Cd(1)−Se(2)	135.75(6)
C(22)−Se(1)−Cd(1)	97.7(3)	C(11)−Se(2)−Cd(1)	94.7(3)
C(5)−O(1)−C(4)	105.8(9)	C(16)−O(2)−C(15)	107.2(10)
C(5)−N(1)−C(3)	108.9(9)	C(16)−N(2)−C(14)	108.5(9)
C(5)−N(1)−Cd(1)	122.9(8)	C(3)−N(1)−Cd(1)	126.6(7)
C(16)−N(2)−Cd(1)	124.1(8)	C(14)−N(2)−Cd(1)	126.4(7)

Table 4. Significant Bond Lengths (Å) and Angles (deg) for **3**

Hg−N(2)	2.469(9)	Hg−N(1)	2.515(8)
Hg−Se(1)	2.479(2)	Hg−Se(2)	2.4764(14)
Se(1)−C(1A)	1.920(12)	Se(2)−C(1B)	1.906(14)
O(1)−C(7A)	1.351(11)	O(1)−C(8A)	1.434(13)
O(2)−C(7B)	1.353(13)	O(2)−C(8B)	1.45(2)
N(1)−C(7A)	1.249(12)	N(1)−C(9A)	1.484(12)
N(2)−C(7B)	1.25(2)	N(2)−C(9B)	1.494(14)
N(2)−Hg−Se(2)	86.2(2)	N(2)−Hg−Se(1)	116.0(2)
Se(2)−Hg−Se(1)	147.66(5)	N(2)−Hg−N(1)	98.1(3)
Se(2)−Hg−N(1)	115.2(2)	Se(1)−Hg−N(1)	86.1(2)
C(1A)−Se(1)−Hg	102.6(3)	C(1B)−Se(2)−Hg	103.3(3)
C(7A)−O(1)−C(8A)	106.3(8)	C(7B)−O(2)−C(8B)	106.0(9)
C(7A)−N(1)−C(9A)	110.0(8)	C(7A)−N(1)−Hg	123.7(7)
C(9A)−N(1)−Hg	123.1(6)	C(7B)−N(2)−C(9B)	107.0(9)
C(7B)−N(2)−Hg	126.0(7)	C(9B)−N(2)−Hg	124.5(8)

Molecular Structure of Compound 2. The colorless crystals of the Cd(II) complex **2** belong to the space group *Pbca* of the orthorhombic system. A PLUTO[33] plot of the structure is shown in Figure 4, and significant bond lengths and angles are given in Table 3. The geometry around the metal center is distorted tetrahedral. The average Cd−Se bond length 2.550(2) Å lies intermediate between terminal Cd−Se [2.483(3) Å] and bridging Cd−Se [2.599(4) Å] values reported in the literature.[34] The average Cd−N bond distance 2.277(9) Å is, however, significantly shorter than that reported for $\mathrm{Cd(SeNC_5H_4)_2}$ [2.425(2) Å].[6a] The Se−Cd−N chelate ring bite angle is 89.4(2)°. The Se−Cd−Se and N−Cd−N angles are

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Table 5

complex	space group	selected bond length (Å) ⟨M−Se⟩	⟨M−N⟩	⟨Se−C⟩	chelate ring bite angle ⟨Se−M−N⟩ (deg)	interplanar angle Se−M−Se/N−M−N (deg)
1	$P2_1$	2.378(1)	2.048(6)	1.890(8)	97.0(2)	72.1(3)
2	*Pbca*	2.550(2)	2.277(9)	1.940(11)	89.4(2)	71.0(3)
3	$P2_1/c$	2.478(1)	2.492(8)	1.913(13)	86.2(2)	69.9(3)

135.7(5) and 105.0(4)°, respectively. The interplanar angle between Se−Cd−Se and N−Cd−N is 71.0(3)°.

Molecular Structure of Compound 3. The mercury complex **3** crystallizes in the monoclinic system of space group $P2_1/c$ with two molecules per unit cell. An ORTEP view of **3** is shown in Figure 5, and significant bond lengths and angles are given in Table 4. The average Hg−Se bond length 2.478(1) Å is normal and close to the previously reported values.[35] The Hg−N bond length of 2.492(8) Å is, however, considerably shorter than those reported in the literature for the related structures of $Hg(SeNC_5H_4)_2$ [2.984(1) Å][6a] and $Hg(SeC_6H_4CH_2NMe_2\text{-}2)_2$ [2.648(20) Å].[9] The chelate bite angle is slightly less [86.2(2)°] in the present case as compared with that in the $Hg(SeC_6H_4CH_2NMe_2\text{-}2)_2$ complex [90.1(4)°]. The Se−Hg−Se angle [147.6(3)°] is considerably lower than that observed for $Hg(SeC_6H_4CH_2NMe_2\text{-}2)_2$ [159.6(3)°], whereas the N−Hg−N angle [98.1(4)°] is comparable to that of the latter case [98.7(6)°]. The interplanar angle is found to be 69.9(3)°; the corresponding average value in the $Hg(SeC_6H_4CH_2NMe_2\text{-}2)_2$ complex is 89.5(10)°.

It is worth comparing the salient structural features of the series (Table 5): (i) The chelate bite angle decreases as the size of the metal ion increases from Zn to Hg. (ii) The interplanar angles between the Se−M−Se and N−M−N planes also decrease down the group, indicating a relatively large distortion from the tetrahedral geometry. (iii) As expected, the M−N bond distances increase in going from Zn to Hg due to "hard"−"soft" interactions, whereas, for the M−Se distances, Hg−Se is shorter than Cd−Se and close to Zn−Se, indicating a stronger "soft"−"soft" interaction between Hg and Se. (iv) The six-membered chelate rings in all the three complexes are highly puckered as attempts to fit a mean plane from the six atoms showed large deviations. (v) Interestingly, the conformation of the oxazoline ring varies depending on the metal ion. In case of the zinc complex, both oxazoline rings have an envelope conformation (C_s symmetry) with the C(18) (+0.20(1) Å) and C(28) (−0.34(1) Å) atoms showing the largest deviations from the mean plane of the other four atoms. In contrast, in cadmium and mercury complexes only one of the oxazoline rings has an envelope conformation whereas the other is highly planar. The atoms showing deviations from the oxazoline ring plane are C(4) (−0.26(1) Å) for the Cd complex and C(8A) (+0.16(1) Å) for the Hg complex.

The bond distances and angles for the oxazoline rings in all the cases reflect certain similarities with other five-membered heterocycles containing O and N atoms such as isoxazoline[36] and oxazolo[37] compounds. The O(1)−C(17) length [1.362(8) Å] in complex **1** is significantly shorter than the O(1)−C(18) bond distance [1.420(10) Å], while the same is true for the N(1)−C(17) distance [1.302(9) Å] with respect to the N(1)−C(19) bond distance [1.472(10) Å]. This indicates a similar double-bond character in both O(1)−C(17) and N(1)−C(17). Complexes **2** and **3** show similar properties.

Conclusion

The intramolecularly coordinating 2-(4,4-dimethyloxazolino)-benzeneselenolate ligand facilitates the isolation of a series of monomeric four-coordinate group 12 selenolate complexes, including the rare example of a "helically" chiral zinc complex. In contrast to the polymeric selenolates generally obtained for group 12 metals, these complexes are monomeric and the degree of association is controlled by the internal chelation of the oxazoline ligand. The formation of the six-membered chelate ring in each case seems to be an important factor in deciding the molecular nature of these compounds. In addition, the bidentate selenolate ligand can be used to prepare helically chiral metal complexes. The monomeric complexes studied here do not undergo association in polar solvents. The incorporation of the oxazoline ring with potentially diastereotopic protons not only allows the use of ^1H NMR to determine the presence of helicity in the complexes but also improves the solubility of the complexes in hydrocarbon solvents.

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Supporting Information Available: Figures showing the room-temperature ^{77}Se NMR spectrum of **1**, mass spectra for **1**−**3**, and TGA and DTA of **1**−**3**, along with complete tables of crystallographic data, final atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen atom coordinates (28 pages). Ordering information is given on any current masthead page.

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